

# Standard Reference Data for the Viscosity of Toluene

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Viscosity is an important transport property for the optimum design of a chemical process plant and for the development of molecular theories of the liquid state. A large amount of experimental viscosity data has been produced for all types of liquids, from alternative refrigerants to molten salts and molten metals. The accuracy of these data is related to the operating conditions of the instrument and, for this purpose as well as for the calibration of relative instruments, standard reference data for viscosity are necessary over a wide range of temperatures. New experimental data on the viscosity of liquid toluene along the saturation line have been obtained recently, mostly at low temperatures. The quality of the data is such that recommended values can be proposed with uncertainties of 0.5% (95% confidence level) for  $260\text{ K} \leq T \leq 370\text{ K}$  and 2% for  $210\text{ K} \leq T < 260\text{ K}$  and  $370\text{ K} < T \leq 400\text{ K}$ . A discussion about the uncertainties in the measurements and about the purity of the samples is made. The proposed value for the viscosity of liquid toluene at 298.15 K and 0.1 MPa is  $\eta = 554.2 \pm 3.3\text{ }\mu\text{Pa s}$ . © 2006 American Institute of Physics. [DOI: 10.1063/1.1928233]

Key words: liquid; reference material; toluene; viscosity.

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## 1. Introduction

In recent papers<sup>1–4</sup> standard reference data for the thermal conductivity of liquid toluene, liquid water, liquid n-heptane, and liquid benzene for most of the normal liquid range have been proposed. The available data in the literature were assessed by a careful analysis of the experimental methods, sample purity, and equipment used and divided into primary and secondary data. The primary data were used to develop correlations for the thermal conductivity of toluene, water, and n-heptane, along the saturation line as a function of temperature. This work<sup>1–4</sup> was carried out under the auspices of the Subcommittee on Transport Properties, of the Commission on Thermodynamics, within the International Union of Pure and Applied Chemistry, and was published later for toluene, water, and n-heptane as part of a complete set of recommendations on the different physicochemical properties of fluids by IUPAC.<sup>5</sup>

Toluene is in the liquid state under its saturation pressure over a very wide range of temperature and is, therefore, a desirable calibrating reference material for many properties as it can be obtained with a high purity. (The liquid range for toluene is from  $T_{tr}=178.15$  K to  $T_{cr}=593.95$  K. The normal boiling point temperature is  $T_{nbp}=383.764$  K. These data were taken from Goodwin.<sup>22</sup>) This paper presents correlations and proposes standard reference data for the viscosity of toluene between 210 and 400 K. Over this range, it varies by a factor of 5. To the knowledge of the authors, standard reference data have not been proposed for the viscosity of toluene over a wide temperature range, nor for other recommended fluids with metrological interest, with the exception of water at 20 °C for which the value of Swindells *et al.*<sup>6</sup> was later endorsed by ISO<sup>7,8</sup> and IUPAC.<sup>5</sup>

The viscosity of liquids is highly dependent on temperature and purity, and can vary by a factor of ten powers of 10. It is therefore very important to produce standard reference data and certified reference materials for the calibration of the viscometers used in science and industry that do not use an absolute method of measurement, in order to provide traceability of the data produced, for scientific and industrial/trade objectives.

This paper presents a correlation based on selected reference data for the viscosity of toluene between 210 and 400 K, at the saturation pressure, as well as recommended values for 298.15 K and at other temperatures in this range.

## 2. Experimental Techniques

The experimental methods used for the measurement of viscosity can be classified as absolute and relative. In the absolute methods, the viscosity must be defined precisely in terms of the measurement parameters (the so-called working equation corresponding to a well-defined model of the experimental measurement). In a second step, the quality of that expression (how correct is the description of the measurement and its departures from all the idealizations involved) and the magnitude of the uncertainty of the measure-

ment parameters can be assessed unambiguously. This statement, used previously in the IUPAC work by the authors on the standardization of thermal conductivity data, is conceptually identical to the recent definition of primary methods by the Comité Consultatif pour la Quantité de Matière, BIPM (CCQM) in 1995:<sup>9</sup>

“a primary method of measurement is a method having the highest metrological qualities, the operation of which can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units, and whose results are, therefore, accepted without reference to a standard of the quantity being measured.”

Strictly speaking, there is no primary method at present for the measurement of the viscosity of liquids, as the absolute methods developed so far in order to achieve high accuracy involve the use of instrument constants obtained through experimental calibration. However, the analysis of such methods (designated as relative or secondary) shows completely different levels of departure from the accepted definition of a primary method. Therefore, we chose to designate as “quasiprimary” any method for which a physically sound working equation, relating the viscosity to the experimental-measured parameters, is available, but where some of these parameters have to be obtained accurately by an independent calibration with a known standard. Among the existing methods of measurement of viscosity,<sup>10</sup> we can consider as “quasiprimary” the oscillating disk, the vibrating wire, the torsionally oscillating quartz crystal, and the surface light scattering spectroscopy (SLS) methods. In the oscillating disk viscometer, the disk's edge effect must be calibrated. In the vibrating wire viscometer, it is the density and the radius of the wire that are obtained from known values of viscosity (water at 20 °C is normally used). In the torsionally oscillating quartz crystal, the quality factor of the oscillator in vacuum is calculated from other independent measurements of viscosity. In the surface light scattering spectroscopy it is still necessary to have information about the dynamic viscosity of the vapor phase under saturation conditions, which is still difficult in many cases. All these methods will qualify as primary methods, as soon as these actual experimental limitations are solved.

Consequently, the data obtained with these state-of-the-art instruments have smaller uncertainties (or greater accuracies), when compared with data obtained using other secondary methods, namely the capillary viscometer (in any of its versions), the rolling-ball viscometer, or the falling ball viscometer.

## 3. Experimental Data

In this work, we tried to comply with the recommendations previously made<sup>1</sup> for the selection of primary and secondary data for thermal conductivity. The primary data for this property were identified using criteria (i)–(vii), thoroughly discussed in Assael *et al.*<sup>2</sup> As no absolute measurements are available, only the data traceable to the water value at 20 °C of Swindells *et al.*,<sup>6</sup> corrected for ITS 90,<sup>8</sup>

TABLE 1. Primary sources of experimental data for the viscosity of liquid toluene

| Literature source                            | Technique <sup>a</sup> | Temperature range (K) | No. of data points | Assigned uncertainty ( $\pm$ %) | Purity class |
|--|------------------------|-----------------------|--------------------|---------------------------------|--------------|
| Bauer and Mehlender (1984) <sup>11</sup>     | CF                     | 293–298               | 3                  | 0.3                             | MPNP         |
| Dymond and Robertson (1985) <sup>12</sup>    | CF                     | 288–393               | 7                  | 0.5                             | DGF          |
| Gonçalves <i>et al.</i> (1987) <sup>13</sup> | CF                     | 298–350               | 6                  | 0.3                             | MPNP         |
| Dymond <i>et al.</i> (1991) <sup>14</sup>    | CF <sup>b</sup>        | 298–373               | 4                  | 0.5                             | MPNP         |
| Kaiser <i>et al.</i> (1991) <sup>15</sup>    | CF                     | 218–378               | 18                 | 0.3                             | MPFP         |
| Krall <i>et al.</i> (1992) <sup>16</sup>     | OD                     | 298–350               | 6                  | 0.5                             | MPNP         |
| Dymond and Simoiu (1996) <sup>17</sup>       | CF                     | 259–318               | 10                 | 0.5–2.0                         | DF           |
| Assael <i>et al.</i> (2000) <sup>18</sup>    | VW                     | 213–363               | 16                 | 0.5                             | DF           |
| Fröba and Leipertz (2003) <sup>19</sup>      | SLS                    | 263–383               | 13                 | 1.0                             | MPNP         |

<sup>a</sup>CF=capillary flow; OD=oscillating disk; VW=vibrating wire; SLS=surface light scattering.

<sup>b</sup>The atmospheric pressure viscosities were measured by special suspended-level capillary viscometer with an accuracy of 0.5%. For toluene, measurements had been made at 298, 323, and 348 K. The reported value at 373 K was, in fact, not experimental, but obtained by extrapolation for calculation of viscosity ratios.<sup>43</sup>

were selected as primary data. Therefore the criteria applied for thermal conductivity were modified to read as follows:

- (1) viscometer calibrated with water which had been distilled at least once;
- (2) water viscosity data from Swindells *et al.*,<sup>6</sup> with variation of temperature given by the ISO standards,<sup>7,8</sup> or any other source, provided that the values used are known, so that corrections can be applied;
- (3) a statement of accuracy was made by the author, or can be inferred;
- (4) the sample purity is stated;
- (5) the data dispersion when fitted to the polynomial Eq. (1) is smaller than the accuracy; and
- (6) the descriptions of the measuring method and the experimental conditions are unambiguous.

The quality of the available experimental data allows the imposition of a limiting accuracy for the primary data of 0.5%, except for the temperature extremes where some points with an estimated accuracy of 1%–1.5% were used.

### 3.1. Purity of Samples Used

Toluene is known to be a hygroscopic material and a very good solvent for nonpolar organic materials. It is therefore important to consider the purity of the samples used by the different authors, in particular those that contribute to the primary data sets.

Among the main impurities, water is one of the major concerns because of its high value of viscosity, and its strong solubility in most liquids. Benzene is the other most common impurity. Impurities can be removed through fractional distillation or, for water in particular, resorting to the use of calcium hydride, or molecular sieves, that remove water to a ppm level.

Therefore, whenever available, the purity of the samples used by the different authors is presented in Table 1, and the samples are classified as follows: manufacturers stated purity, no further purification (MPNP); manufacturers stated purity, further purification (MPFP); dried with molecular

sieves, silica gel or phosphorous pentoxide (D); dried and filtered sample (DF); degassed and filtered sample (DGF); and purified and dried samples with GC or GC–MS analysis (PDSA).

In all the cases, the purity of the samples exceeds 99.5% for nonpurified samples, and is better than 99.9% for purified and dried samples.

### 3.2. Primary Data

A summary of primary data for toluene, together with their estimated accuracy and purity classification is given in Table 1. The statistical treatment of data is the same adopted in previous work.<sup>1–4</sup> In this table, the accuracy assigned is that claimed by the authors, since most equipment operates along the saturation line of the liquids, or at a pressure of 0.1 MPa, and the standard reference values refer to these conditions, therefore no extrapolations were necessary. In practice, there is no distinction between the values of the viscosity over the range of conditions presented here, except for the data above 380 K, which has to be considered to refer to the saturation line, because the vapor pressure is then greater than 0.1 MPa. However, a change in pressure of 0.1 MPa will not change the viscosity of toluene by more than 0.08%. Consequently, the difference between the viscosity at 393 K for the saturation line and at 0.1 MPa is less than 0.04% and is insignificant.

Some comments about the data sets used are necessary, as all the experimental data prior to 1990, and even some obtained after that date, relate to temperatures on IPTS 68. The exceptions are the data of Assael *et al.*,<sup>18</sup> and Fröba and Leipertz,<sup>19</sup> which were measured on the ITS 90. The differences in temperature scales over the temperature range used in this work are never larger than 30 mK. The effect in the reported viscosities never exceeds  $5.3 \times 10^{-7}$  Pa s (10 mK at 213 K) and is only  $6.5 \times 10^{-8}$  Pa s (30 mK at 393 K), which is well below the uncertainty of the reported data. Despite this, and for the sake of consistency, all the temperatures on

ITPS 68 were corrected to ITS 90 using the corrections proposed by Preston-Thomas,<sup>20</sup> and therefore the correlations presented in Sec. 4 are based on the ITS90.

For all the methods used, the kinematic viscosity can only be obtained if the density of the liquid at the experimental thermodynamic state is known, so for consistency, the densities used by the different authors were replaced by densities calculated by Eq. (2) in the paper by Magee and Bruno<sup>21</sup> for temperatures up to 273.15 K, and Goodwin's equation of state (EOS) (NIST)<sup>22</sup> using the FORTRAN code supplied by NIST, for temperatures higher than 273.15 K.

The data of Bauer and Meerlender<sup>11</sup> were obtained with capillary master viscometers calibrated with water and standard oils, and the raw measurements corrected for surface tension, buoyancy, kinetic energy, and temperature effects. The temperature was measured with a 0.1 mK resolution, and toluene of purity better than 99.5% by GLC as stated by the manufacturer, from two different suppliers was used. The data of Dymond and Robertson<sup>12</sup> were obtained with a capillary viscometer with buoyancy, kinetic energy, and temperature effects being considered. Toluene of 99.95% purity, by GLC according to the manufacturer, was used after degassing and filtering and the temperature was controlled to better than 0.02 K. Gonçalves *et al.*<sup>13</sup> used a capillary viscometer calibrated with water. The kinetic energy correction was accounted for. Water viscosities and densities for the calibration of the viscometers were obtained from IAPS Formulation 1984. The accuracy was estimated at 0.3%. The toluene purity was better than 99.9% by GLC, as stated by the manufacturer. The temperature, which was measured to 0.1 K, was constant to 0.02 K. Dymond *et al.*<sup>14</sup> used two suspended-level capillary viscometers, having different capillary bores and capillary lengths, to get an estimate of the accuracy of their measurements, which were traceable to water calibration in a Master viscometer, at the National Engineering Laboratory, East Kilbride, Glasgow. The reported value at 373.15 K was obtained by extrapolation for use in calculating viscosity ratios of the high-pressure data to the atmospheric value. The toluene purity was 99.9% by GLC according to the manufacturer. The data of Kaiser *et al.*<sup>15</sup> were obtained with capillary viscometers calibrated with standard oils from Physikalische Technische Bundesanstalt, Germany (PTB) to 0.28%. Surface tension, buoyancy, kinetic energy, and temperature effects were accounted for. The temperature stability was 0.02 K, and the estimated accuracy was 0.1–0.2 K. The toluene had a purity greater than 99%, as stated by the manufacturer's GLC, was dried, and distilled under vacuum but its purity was not determined afterwards. The data of Krall *et al.*<sup>16</sup> were obtained with an oscillating disk viscometer calibrated with water, with an accuracy of 0.5%. The toluene purity was 99.9% by GLC, according to the manufacturer. The temperature was measured with a resolution of 0.03 K, and an accuracy of 0.1 K. Dymond and Simoiu<sup>17</sup> used a capillary master viscometer, calibrated with de-ionized water, correcting only the kinetic energy effect. The toluene purity was greater than 99.9% by GLC, as stated by the manufacturer, and dried using molecular sieve 4A.

The temperature was controlled to 0.01 K and measured with a calibrated platinum resistance thermometer, whose resolution and accuracy were not stated. Assael *et al.*<sup>18</sup> used a vibrating wire viscometer, calibrated with water, with an accuracy of 0.5%. The toluene purity was 99.9%, as stated by the manufacturer prior to purification. After purification, no purity was stated, except for the reduction of water content from 200 to 100 ppm. The temperature was measured with an accuracy of 0.01 K. Toluene densities were calculated from the data of Magee and Bruno.<sup>22</sup> Fröba and Leipertz<sup>19</sup> used a revised SLS, with accuracy better than 1%. The toluene purity was better than 99.9% according to the manufacturer and the sample was used without further purification. The temperature was measured in ITS 90 with accuracy better than 0.015 K. Toluene densities were calculated from the data of Goodwin.<sup>22</sup>

### 3.3. Secondary Data

As secondary data we considered 16 sets. A summary of the secondary data sets for toluene, together with their estimated accuracy and purity classification, is given in Table 2. The uncertainty, when available, is the author's claimed value. The purity is also the claimed purity, normally assigned by GLC.

The data of Lima,<sup>23</sup> Mamedov and Panchenkov,<sup>24</sup> and Hammond *et al.*<sup>25</sup> were obtained with capillary viscometers. Neduzhii and Khmara<sup>26</sup> used a capillary transpiration viscometer, without mentioning temperature accuracy or resolution. The dynamic viscosity was calculated using toluene densities determined experimentally resorting to the viscometer employed as a pycnometer, but the density values were not reported, and therefore could not be recalculated with the density data used in the present work. The toluene purity was 99.74%, determined by GLC, and the data reported are smoothed, without mention either of raw data or fitting equation parameters. The accuracy is better than 3%, and probably about 1.5%. The data of Akhundov *et al.*<sup>27</sup> were obtained with a capillary viscometer, for toluene of 99.96% purity. Temperature was controlled and measured to 0.01 K with a platinum resistance thermometer.

Karbanov and Geller<sup>28</sup> used a capillary viscometer, with the temperature measured to within 0.02–0.03 K. Medani and Hassan<sup>29</sup> used a rolling-ball viscometer, with no accuracy statement. Teja and Rice<sup>30</sup> determined their data with a capillary viscometer. The data of Kashiwagi and Makita<sup>31</sup> were obtained with a torsionally oscillating quartz crystal viscometer calibrated with 14 fluids: two "viscosity standard liquids" from National Research Laboratory of Metrology, Japan (NRLM) and 12 hydrocarbons of known viscosity (including toluene itself), using a least squares fit. Toluene of commercial reagent grade, with a stated purity of not less than 99%, not tested by any means, was used without purification. The uncertainty was estimated to be less than 2%, based on a maximum deviation of about 1% between the measured and literature values for the 14 calibrating fluids. The temperature was measured in terms of IPTS-68 with a



TABLE 2. Secondary sources of experimental data for the viscosity of liquid toluene

| Literature source                               | Technique <sup>a</sup> | Temperature range (K) | No. of data points | Claimed uncertainty ( $\pm$ %) <sup>c</sup> | Purity of samples used (%) |
|---|------------------------|-----------------------|--------------------|---|----------------------------|
| Lima (1952) <sup>23</sup>                       | CF                     | 293–353               | 7                  | 2.4   | N/A                        |
| Mamedov and Panchenkov (1955) <sup>24</sup>     | CF                     | 253–353               | 11                 | N/A   | N/A                        |
| Hammond <i>et al.</i> (1958) <sup>25</sup>      | CF                     | 293–353               | 7                  | 0.2   | N/A                        |
| Neduzhii and Khmara (1968) <sup>26</sup>        | CT                     | 220–360               | 15 <sup>b</sup>    | 1.5–3                                       | 99.74                      |
| Akhundov <i>et al.</i> (1970) <sup>27</sup>     | CF                     | 296–373               | 4                  | 1.2   | 99.96                      |
| Karbanov and Geller (1975) <sup>28</sup>        | CF                     | 193–363               | 15                 | 1.8–2                                       | 99.95                      |
| Medani and Hassan (1977) <sup>29</sup>          | RB                     | 353–453               | 12                 | N/A   | N/A                        |
| Teja and Rice (1881) <sup>30</sup>              | CF                     | 298–323               | 3                  | N/A   | N/A                        |
| Kashiwagi and Makita (1982) <sup>31</sup>       | TOQC                   | 298–323               | 4                  | $\leq 2\%$                                  | > 99                       |
| Sing and Sinha (1984) <sup>32</sup>             | CF                     | 290–333               | 5                  | N/A   | N/A                        |
| Ritzoulis <i>et al.</i> (1986) <sup>33</sup>    | CF                     | 288–308               | 3                  | N/A   | N/A                        |
| Byers and Williams (1987) <sup>34</sup>         | CF                     | 298–368               | 8                  | 0.5   | > 99                       |
| Diller and Jung (1989) <sup>35</sup>            | TOQC                   | 185–320               | 19                 | 3%  | > 99.97                    |
| Et-Tahir <i>et al.</i> (1995) <sup>36</sup>     | CF                     | 298–363               | 5                  | 1%  | > 99.5                     |
| Santos and Nieto de Castro (1997) <sup>37</sup> | TOQC                   | 298–373               | 4                  | 0.5%  | > 99.99                    |
| Caetano <i>et al.</i> (2004) <sup>38</sup>      | DVW                    | 213–298               | 15                 | 1–1.5%                                      | > 99.99                    |

<sup>a</sup>CF=capillary flow; CT=capillary transpiration; RB=rolling ball; TOQC=torsionally oscillating quartz crystal; DVW=dual vibrating wire.

<sup>b</sup>Author fitted data points.

<sup>c</sup>N/A=not available.

SPRT calibrated at NRLM with accuracy better than 20 mK, but neither the measurement resolution nor the accuracy are stated. This method also requires the fluid density in order to calculate the viscosity but no mention is made of the density values used. Singh and Sinha,<sup>32</sup> and Ritzoulis *et al.*,<sup>33</sup> also used capillary viscometers. Byers and Williams<sup>34</sup> used a capillary viscometer calibrated with water, and also used toluene as a secondary calibrant. The toluene purity was better than 99% by GLC, as stated by the manufacturer. The temperature was constant to 0.02 K and measured to 0.1 K. Densities were measured to 0.3%, and kinematic viscosities to 0.5%, so the dynamic viscosities were accurate to 0.8%. The reported temperatures were rounded to the nearest 0.1 K: 298.15 K as 298.2 K. Diller and Jung<sup>35</sup> used a torsionally oscillating quartz crystal viscometer. The toluene purity was greater than 99.9% by GLC, as stated by the manufacturer, and used without further purification. Toluene densities were calculated from Goodwin EOS.<sup>22</sup> The calibration of the quality of the resonant crystal was not done; the experimental value determined in vacuum was used. This type of approach causes big errors, because the energy applied to the crystal cannot be dissipated in a vacuum, and therefore it produces heating effects on the crystal, making it impossible to define the reference temperature. Et-Tahir *et al.*<sup>36</sup> used a capillary viscometer with temperature controlled to 0.1 K, and an estimated accuracy of 1%. The toluene purity was greater than 99.5% by GLC, as stated by the manufacturer. Vieira dos Santos and Nieto de Castro<sup>37</sup> measured the viscosity of toluene with a torsionally oscillating quartz crystal, for temperatures between 298.15 and 373.15 K, and pressures up to 200 MPa. The accuracy of the temperature measurement was 10 mK and the pressure measurement accuracy was 0.4 MPa. A

toluene sample with a nominal purity of 99.5% was treated by fractional distillation under dry nitrogen, and the purity determined by gas chromatography-mass spectrometer (GC-MS) analysis confirmed purity in excess of 99.99%. The quality factor of the oscillator in vacuum was not determined in vacuum but calculated from measurements with toluene from other authors, namely Gonçalves *et al.*<sup>13</sup> This procedure did not contribute to the overall uncertainty of the measurements by more than 0.03%. The accuracy of the data was estimated to be 0.5%. However, as the measurements of the quality factor in vacuum were not traceable to water, these data were considered secondary. Recently Caetano *et al.*<sup>38</sup> improved the operation of their vibrating wire viscometer, by developing a dual vibrating wire technique, operating the vibrating wire sensor in both forced and decay modes. The mutual consistency of the results obtained by the two modes of operation was verified for the entire temperature range and several pressures, the differences between the results obtained by the two modes not exceeding  $\pm 0.4\%$ . The estimated overall uncertainty of the data is estimated to be within 1% at temperatures above 273 K and 1.5% above this temperature. The toluene sample, with manufacturer purity of 99.8%, was dried with molecular sieves and filtered, before being introduced into the vessel under vacuum. Karl-Fischer titration analysis showed final water content smaller than 10 ppm. Toluene densities were calculated by a correlation developed by Assael *et al.*,<sup>39</sup> based on a Tait-type equation, with an accuracy of 0.1%. Although these data have, in principle, an uncertainty compatible with the chosen primary data sets they cannot be considered primary because the data are not traceable to water.

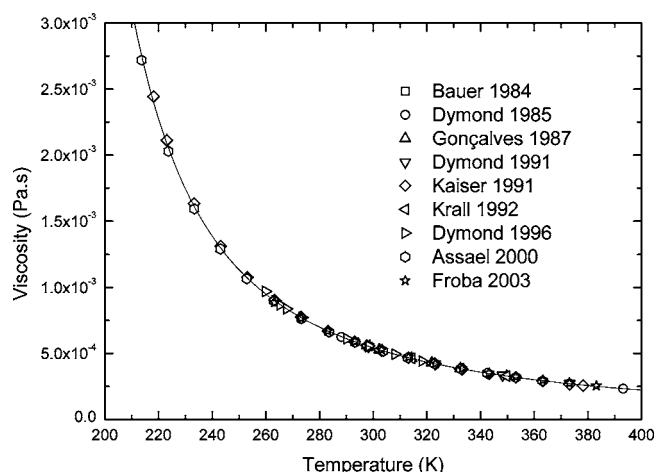


FIG. 1. The primary data selected for the viscosity of toluene along the saturation line, for  $213\text{ K} < T < 393\text{ K}$ . The line represents the proposed reference correlation [Eq. (1)].

## 4. Correlation Procedures and Results

### 4.1. Equation Form

The IAPS formulation for the transport properties of water as developed by Sengers *et al.*<sup>40</sup> and Kestin *et al.*<sup>41</sup> was used in the form:

$$\ln(\eta^*) = A + \frac{B}{T^*} + \frac{C}{(T^*)^2} + \frac{D}{(T^*)^3}, \quad (1)$$

where  $\eta^*$  and  $T^*$  are the dimensionless variables defined as:

$$T^* = T/298.15 \quad (2)$$

$$\eta^* = \eta(T)/\eta(298.15) \quad (3)$$

and

$$\eta(298.15) = 554.2 \pm 3.3 \text{ } \mu\text{Pa.s} \quad (4)$$

is the standard value of the viscosity of toluene at 298.15 K and 0.1 MPa. This value was established from the fit of Gonçalves *et al.*<sup>13</sup> data with Eq. (1), as this data set was considered to be the most accurate one for temperature of 298.15 K.

In order to avoid mathematical dependencies that in practice would amount to transforming Eq. (1) into a five-parameter equation, where the meaning of the reference viscosity would be lost, it was decided that the value obtained from fitting Gonçalves *et al.*<sup>13</sup> data with Eq. (1) would be the reference value.

This equation, capable of describing most of the experimental data sets within their own stated accuracy, for temperatures from 210 to 400 K, was established with nine data sets composed of 83 data points and four different measurement techniques, as summarized in Table 1 and represented in Fig. 1:

$$\ln(\eta^*) = -5.2203 + \frac{8.964}{T^*} - \frac{5.834}{(T^*)^2} + \frac{2.089}{(T^*)^3}. \quad (5)$$

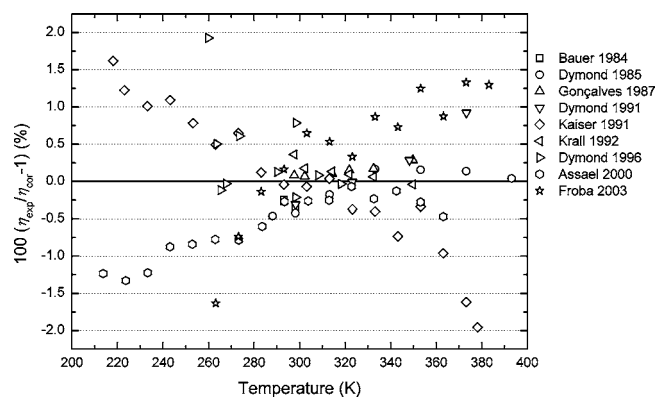


FIG. 2. Deviations of the primary data for toluene from the proposed reference correlation [Eq. (1)].

The maximum deviation of the primary experimental data from the proposed correlation is  $-2\%$ , as shown on the deviation plots of the primary data from the correlation expressed by Eq. (5) given in Fig. 2. The absolute uncertainty of the data calculated directly from this fit, using ISO definition ( $k=2$ ), is  $6.9 \text{ } \mu\text{Pa.s}$ .

Figure 3 shows the deviations of the secondary data, not included in the correlation, from Eq. (5). The data of Vieira dos Santos and Nieto de Castro<sup>37</sup> do not depart from the correlation by more than  $-0.47\%$  at 373.15 K and  $0.28\%$  at 298.15 K, after the densities then used were corrected for the new correlation, the NIST equation of state.<sup>20,21</sup> The most recent data of Caetano *et al.*<sup>38</sup> also agree very well with the correlation proposed, not only for this region, but over the whole temperature range.

In Fig. 4 we present the proposed uncertainty of the data in the different temperature intervals, consistent with Table 2. In the range 220–260 K the sets of Kaiser *et al.*<sup>15</sup> and Assael *et al.*<sup>18</sup> have opposite deviations from the proposed correlation. A single point of Fröba and Leipertz<sup>19</sup> seems to corroborate the tendency of the data of Assael *et al.*,<sup>18</sup> but with a relative deviation of  $-1\%$ .

For the temperature range between 370 and 393 K, we have four different data sets from three authors: Dymond

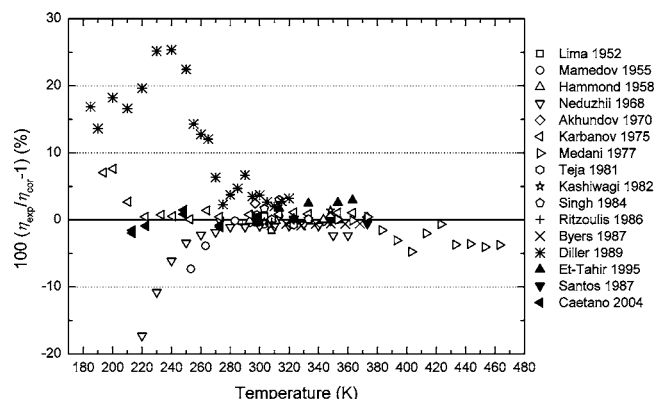


FIG. 3. Deviations of the secondary data published after 1952 for toluene from the proposed reference correlation [Eq. (1)].

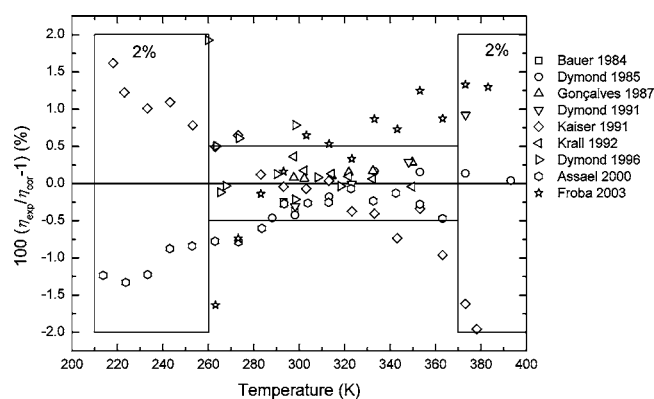


FIG. 4. Accuracy limits of the proposed reference correlation.

*et al.*,<sup>12,14</sup> Kaiser *et al.*,<sup>15</sup> and Fröba and Leipertz.<sup>19</sup> The only high temperature data set by Medani *et al.*<sup>31</sup> agrees with Kaiser data up to 370 K. Finally for the range 393–430 K, the secondary data of Medani *et al.*<sup>31</sup> suggest that we could extend the validity of the correlation, although based on just one secondary data set. It should be noted that the normal boiling temperature for toluene is 383.764 K (ITS-90),<sup>22</sup> so this last range is already for pressure above 0.1 MPa.

There is no noticeable correlation or deviation between the different viscosity measurement methods and their deviations from the correlation.

#### 4.2. Comparison with Previous Correlations

The only available correlation at the saturation pressure was the one established by Kaiser *et al.*<sup>15</sup> for their own data, which covers temperatures from 218 to 378 K. Those authors did not include any other data in their correlation, although they made a thorough comparison with available literature data.

The average and maximum deviations between the two correlations are 2.3 and 15.1  $\mu\text{Pa s}$ , values higher than the assigned accuracy of the data. The deviation maxima are located at the temperature extremes, reflecting a small difference in curvature between the two equations. This agreement was obtained after converting kinematic viscosities generated by the correlation of Kaiser *et al.*<sup>15</sup> into dynamic viscosities, using toluene densities calculated from Goodwin's (NIST) toluene EOS.<sup>22</sup>

#### 4.3. Tabulations

Table 1 summarizes the selected data sets and their more significant properties and Table 2 summarizes the secondary data sets.

Table 3 gives the recommended values for the viscosity of toluene along the saturation line. The recommended values are presented on four or three significant figures but it should be noted that the uncertainties in the tabulated data are based on the analysis made in Sec. 4.1. We estimate the tabulated standard reference data for the viscosity of toluene to have

TABLE 3. Recommended viscosities for toluene

| $T$ (K) | $\eta/\mu\text{Pa s}$ | $T$ (K) | $\eta$ (mPa s) |
|---------|-----------------------|---------|----------------|
|         | $\pm 0.5\%$           |         | $\pm 2\%$      |
| 260     | 949.2                 | 210     | 3.11           |
| 265     | 874.3                 | 215     | 2.67           |
| 270     | 808.7                 | 220     | 2.28           |
| 275     | 750.8                 | 225     | 1.98           |
| 280     | 699.4                 | 230     | 1.75           |
| 285     | 653.5                 | 235     | 1.55           |
| 290     | 612.4                 | 240     | 1.39           |
| 295     | 575.3                 | 245     | 1.25           |
| 300     | 541.8                 | 250     | 1.14           |
| 305     | 511.3                 | 255     | 1.04           |
| 310     | 483.5                 |         |                |
| 315     | 458.1                 | 375     | 0.266          |
| 320     | 434.8                 | 380     | 0.257          |
| 325     | 413.3                 | 385     | 0.247          |
| 330     | 393.5                 | 390     | 0.239          |
| 335     | 375.1                 | 395     | 0.230          |
| 340     | 358.1                 | 400     | 0.220          |
| 345     | 342.3                 |         |                |
| 350     | 327.5                 |         |                |
| 355     | 313.7                 |         |                |
| 360     | 300.9                 |         |                |
| 365     | 288.8                 |         |                |
| 370     | 277.5                 |         |                |

uncertainties of 0.5% (95% confidence level) for  $260\text{ K} \leq T \leq 370\text{ K}$  and 2% for  $210\text{ K} \leq T < 260\text{ K}$  and  $370\text{ K} < T \leq 400\text{ K}$ , as displayed in Fig. 4.

#### 4.4. Caution in the Use of the Tabulated Recommended Viscosities

As previously mentioned,<sup>1–4</sup> recommended standard values serve two purposes: (i) they act as a test of the accuracy of new absolute instruments and (ii) they are a means of calibrating instruments for which the full working equation is not available. It is for the latter use that caution must be used, as the use of toluene alone for the calibration of such instruments may lead to erroneous results for other systems, where the surface tension, kinematic energy correction, buoyancy, and temperature effects will be different. Thus, it is stressed that any relative instrument should be calibrated with at least two fluids with sufficiently different density and surface tension values.

### 5. Conclusions

New standard reference data for the viscosity of toluene based on ITS-90 are proposed, which cover most of the normal liquid range along the saturation line, from 210 up to 400 K. (The melting point of toluene is  $T_m = 178.166\text{ K}$ .<sup>42</sup>) These recommendations are based on selected data obtained with four different methods. The data covers a much wider range in temperature than that proposed in 1998 by ISO.<sup>8</sup> Calibration of viscometers for a wider range in temperature can now be possible, namely above 330 K.

The proposed value of the viscosity of toluene at 298.15 K has an estimated uncertainty of 3.3  $\mu\text{Pa s}$ , or 0.6%. The proposed tabulated data have estimated uncertainties of 0.5% for  $260\text{ K} \leq T \leq 370\text{ K}$  and 2% for  $210\text{ K} \leq T < 260\text{ K}$  and  $370\text{ K} < T \leq 400\text{ K}$  (95% confidence level).

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